

Final Report

Enhanced Oil Recovery from Oil-Seawater Mixtures Through the Coupling of Magnetic Nanoparticles and Electrically Conducting Ultrafiltration Membranes

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Executive Summary

In this project we demonstrated the ability of a membrane-based oil/seawater separation method to remove a large fraction of the water from an oil/seawater mixture without suffering from membrane fouling, which typically limits the use of membranes for oily water treatment. The separation method relies on the formation of Pickering emulsions using magnetic nanoparticles; the nanoparticles partition to the oil/water interface, forming a tight shell around oil droplets that prevents oil coalescence and membrane fouling. Once the water is separated from the oil, a magnetic drum separator is used to recover the nanoparticles that are then recycled and reused to form new Pickering emulsions. We show that the system can handle oil concentrations of 30 g/L in seawater at 2 °C, with the membranes suffering little fouling at fluxes up to 70 L/m² hr. We successfully use polyacrylonitrile ultrafiltration membranes in both flat sheet and spiral wound configurations, with average oil concentrations in the membrane permeate measured at 7 ± 3 ppm, with an average turbidity of 0.1 NTU. A detailed techno-economic analysis shows that the system can be used to drastically reduce oily-water storage needs aboard oil-spill response vessels, by treating oily water remaining after the mechanical separation of oil and water mixtures collected during skimming activities.

Introduction

The separation of crude oil from seawater remains a challenging prospect during oil spill cleanup operations. One of the main methods used to physically remove spilled oil from the ocean surface is through the operation of skimming vessels that use special skimming devices to scoop up oil floating on the surface. Unfortunately, along with the spilled oil, skimming devices also remove large volumes of water, although recent advances in skimming technologies have greatly reduced the water-to-oil ratio in the collected fluid. The large volumes of water that are collected necessitate large storage capacity on skimming vessels, and ultimately reduce their operational time since vessels must return to shore to unload the contaminated water. Thus, an oil/seawater separation method that can be implemented aboard a skimming vessel would be highly advantageous, as the collected water could be disposed of overboard, reducing the storage capacity on the ship and increasing its operational range and duration.

To dispose the collected seawater overboard into the ocean, the oil concentration must be reduced to concentrations below 15 ppm [1]. While “free” oil, that is oil that floats on the water’s surface, can be removed using gravity separation methods such as hydrocyclones and dissolved air flotation, there exists a large fraction of oil that forms a stable emulsion in the water phase. This emulsion is extremely stable, and can reach concentration in excess of 1 g/L [2, 3]. Gravity-based separation methods are not effective at removing the emulsified oil. The emulsified oil forms droplets in the water phase, with sizes typically in the micrometer range. Ultrafiltration (UF) has been demonstrated to be an effective method to separate the emulsified oil phase from the water, producing an oil-free water phase and a concentrated oil phase. However, membrane fouling remains a serious challenge. When water is pushed through the membrane, the local oil concentration along the membrane rises dramatically, which destabilizes the emulsified oil drops, leading to their coalescence and subsequent deposition on the membrane. This blocks water from passing through the membrane. The cleaning process used for the recovery of membrane functionality requires the use of detergents and hot water. This creates large volumes of waste, operational disruptions, and increased membrane wear. Thus, a fouling free membrane separation process would significantly improve the membrane separation process, leading to operational efficiency and increased performance.

We have developed a fouling-free membrane separation process that relies on the coupling of magnetic Pickering emulsions with UF membranes [4]. Pickering emulsions are emulsions that rely on particles partitioning to the oil/water interface, rather than on amphiphilic molecules (surfactants). The particles form a shell around the oil drop, which prevents neighboring oil drops from coalescing and fouling the membrane. In this way, very high concentrations of oil can be stabilized in seawater (concentrations exceeding 100 g/L are easily achieved). When crude oil Pickering emulsions are treated with a membrane, the stabilized droplets do not coalesce, and the membrane does not foul. Thus, very high recoveries can be achieved, and the membranes can be operated continuously with no cleaning required. The water passing through the membrane is oil-free and can be safely disposed of overboard. Once a large fraction of water is removed from the oil/water mixture, a magnetic field can be used to recover the magnetic nanoparticles (NPs) and they can be reused as oil stabilizing agents.

The objective of this project was to construct a membrane-based oil/water separation system and demonstrate the feasibility of using the treatment technique. The system was designed to operate in a continuous fashion at 90% recovery, while recycling and reusing the magnetic NPs used to stabilize the crude oil. In the context of membrane filtration, the term “90% recovery” means that when treating a given volume of solution (water + oil), the membrane removes 90% of the volume from the oil/water solution, with the remaining 10% of the volume containing all of the initial oil and whatever water is needed to make 10% of the initial volume. For example, if an oil/water mixture contains 3 g/L of oil (i.e. 3 g of oil and 997 g of water), then after the membrane treatment (at 90% recovery), the system would produce a stream of pure water (900 g) and a stream of oil and water (100 g total, with 30 g of oil and 70 g of water). Three different UF membrane configurations were tested: flat sheet, hollow fiber, and spiral wound. The goal of the project was to operate the UF membrane system at high fluxes while minimizing membrane fouling during the treatment of highly contaminated seawater at a temperature of 2 °C meant to

simulate arctic-like conditions. The project was successful in identifying the appropriate operating conditions and operational constraints needed to maintain optimal performance. Further, a detailed techno-economic analysis of the treatment process was performed, and detailed technical plans for a further system scale-up were drafted (see Appendix B).

Materials and Methods

In this project, we designed and built a continuous membrane-based oil/seawater separation process. The separation process relies on the coupling of magnetic Pickering emulsions to membrane filtration, followed by a magnetic separation step that recovers the NPs used to form the Pickering emulsions and recycles them for further use (Figure 1). In an effort to simulate arctic-like conditions, the entire system was constructed inside a walk-in refrigerator maintained at 2 °C. For clarity, we will describe each element of the water treatment system separately.

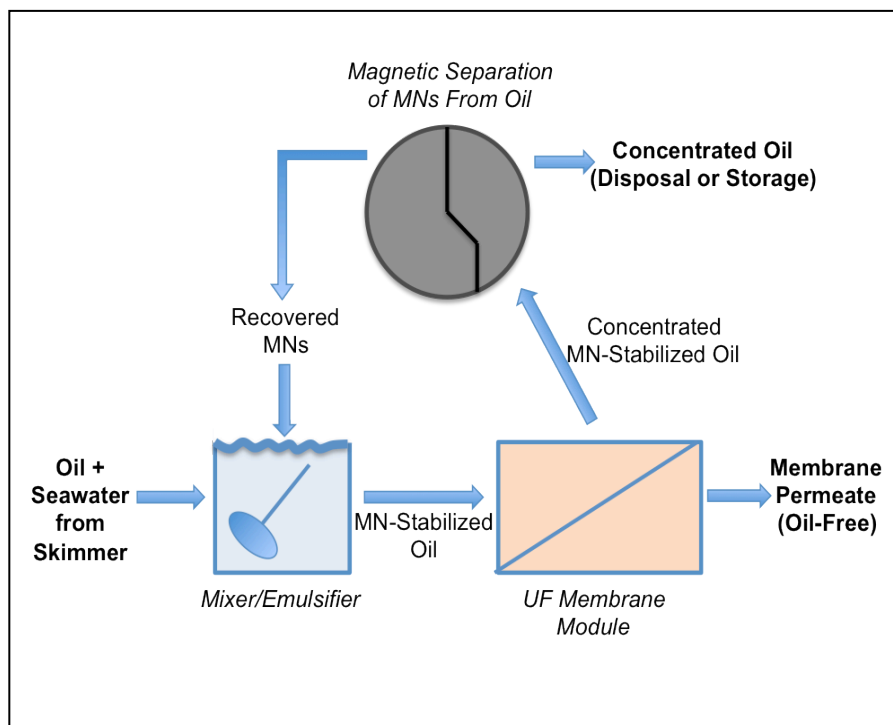


Figure 1. Schematic of oil/water separation process used to remove and recover emulsified oil from seawater.

Materials and chemicals

We tested three types of iron particles: magnetite NPs (Fe_3O_4 , 30-40 nm, purchased from Skyspring Nano), maghemite NPs ($\gamma\text{-Fe}_2\text{O}_3$, 30-40 nm, purchased from Skyspring Nano), and carbonyl iron (CI) microparticles ($\text{Fe}_2(\text{CO})_9$, 2 μm , purchased from Skyspring Nano). Polyacrylonitrile (PAN) membranes (MWCO 75 kDa) in flat sheet and spiral wound configurations were purchased from Nanostone, Inc. (Oceanside, CA). Polyvinylidene fluoride (PVDF) UF membranes (MWCO 150 kDa) in a hollow fiber configuration (HFU-LAB) were

purchased from Toray Industries (Japan). The crude oil (Alaskan North Slope (ANS)) used in this work was kindly provided by the Bureau of Safety and Environmental Enforcement. Synthetic seawater was produced by mixing 35 g/L of InstantOcean into deionized water (DIW).

Pickering emulsion stability

We investigated the three types of iron particles for the purpose of determining the minimum amount of particles needed to form stable and effective Pickering emulsions. Our definition of “stable and effective” is an emulsion that once the oil/particles are removed from the water phase, no emulsified oil remains in the water phase. The following particle/oil ratios (w/w) were tested: 0:1, 0.05:1, 0.1:1, 0.2:1, 0.5:1, 0.75:1, and 1:1. All experiments were done in triplicate, with error bars corresponding to 95% confidence intervals.

To test the different particles and concentrations the following experimental steps were performed:

1. 3 g/L of ANS crude oil were vigorously mixed into synthetic seawater maintained at 2 °C using a paddle mixer at 1,550 RPM for 10 minutes.
2. Different concentrations of iron particles were added to the oil/seawater mixture and the system was vigorously mixed with the paddle mixer at 1,550 RPM for 10 minutes.
3. A small sample was removed, placed on a slide and observed with an optical microscope to determine the average droplet size.
4. A grab sample was removed (using a 40 ml glass vial) and allowed to settle for 60 minutes.
5. A water sample was removed from the middle of the glass vial and the residual oil concentration was evaluated using a total organic concentration (TOC) analyzer.
6. Photos were taken from the side and top of the vial to evaluate whether there was any residual oil floating at the water/air interface.

The *rational* behind our experimental approach is that if the emulsification process was successful, no residual emulsified oil should remain in the aqueous phase, as it will all be entrapped in the particle-stabilized oil drops. In Step 1, we are attempting to mimic the conditions occurring in the ocean after an oil spill, where a fraction of the oil will form a natural emulsion and the majority of oil will remain in the “free” form floating on the surface. In Step 2, we add the iron particles and apply agitation to break up the nanoparticle aggregates, shear the oil phase, and allow the particles to partition to the oil/water interface. In Step 4, 5 and 6, we are testing whether the particles were able to remove all of the oil from the water phase. In Step 3 we used an optical microscope to determine the average particle size. Optical microscopy was sufficient to determine this, due to the relatively large size of the Pickering emulsion droplets. To verify this, we also imaged a limited number of NP-stabilized oil drops with a scanning electron microscope (SEM).

Process control and fluid management

Flow and pressure through the system was maintained using progressing cavity pump; due to the abrasive nature of the NPs used to form the Pickering emulsions, pumps that rely on spinning

blades (such as centrifugal pumps) rapidly degrade and should not be used in the process. A 5-gallon tank was used to hold the feed (oil, water and NPs); the feed tank was continuously stirred at 1,500 rpm using a paddle mixer. Water from the feed tank was fed via the pump to the membrane flow module with the pressure of the membrane system maintained through the opening and closing of a valve on the membrane retentate line; the membrane systems were operated in a constant flux mode, with the flux being maintained by changing the transmembrane pressure. The cross-flow velocity of the system was maintained at approximately 30 cm/s. The membrane systems were periodically backwashed (see Results and Discussion for backwashing intervals and durations) with permeate. No further chemical cleaning was performed on the membranes. Before starting the experiments, the membranes were compressed for at least 24 hours with DIW.

The system was operated in a “closed loop” configuration, where the membrane retentate was recycled and used as the feed for the membrane unit, and the membrane permeate and recovered oil and NPs were returned to the feed tank. A certain volume of retentate was removed via a peristaltic pump and passed to the magnetic separator for oil, NP and water recovery (see below). An equal volume of feed was added to the system (from the feed tank), so that the rate of retentate flowing to the magnetic separator plus the rate of permeate flow was equal to the rate of feed water added to the system, resulting in a constant volume of water cycling through the membranes. This configuration was used in an effort to reduce the volumes of water and crude oil used in the study. Thus, steady-state conditions emerge over time; this steady-state is governed by the rate of permeate and retentate that needs to be replaced to maintain a constant volume in the system. Based on system geometry and flow rates, the concentration of crude oil stabilized in the recycling loop to 10X the concentration in the feed tank. Thus, if the feed is 3 g/L, then the actual concentration (at steady state) in the membrane module is 30 g/L. This is based on a mass balance calculation we performed. This concentration factor is a function of the flux and system volume, and we have developed a calculator that tells us exactly the “real” concentration that the membranes experience. Thus, the conditions tested in this phase of the project are extremely challenging. A picture of the separation system can be seen in Figure 2. Hydraulic parameters were controlled through a series of control algorithms developed by our team using open-source software. The details of the process control methodology are listed in Appendix A. Additionally, a piping and instrumentation diagram describing the system can also be found in Appendix A.

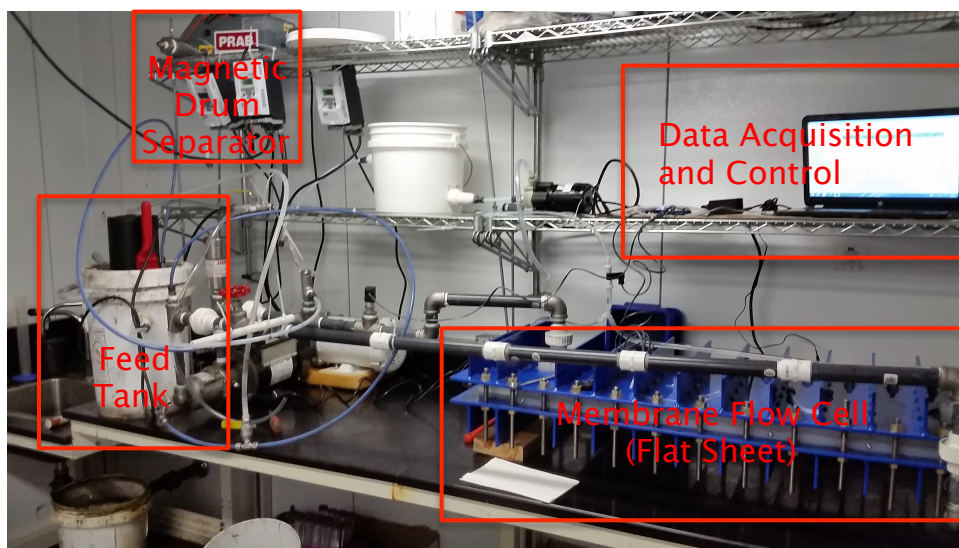


Figure 2. Oil/seawater separation system and individual sub-systems constructed inside cold room.

Separation units

Three different UF membrane configurations were tested – flat sheet, hollow fiber, and spiral wound. Based on our previous work, it was determined that the PAN membranes have the appropriate surface characteristics (hydrophilic with MWCO in the range of UF) to facilitate oil/water separation while operating at high fluxes and minimizing membrane fouling [4]. The initial work was done with the flat-sheet membrane module, and later the other configuration were tested. In all cases, oil-free membrane permeate was returned to the feed tank, and an identical volume was removed from the retentate line and passed to the magnetic separator (see below). The magnetic separator separated NPs from the retentate and the separated streams were also sent back to the feed tank to maintain a completely recycled system.

Flat sheet membrane module: The flat sheet membrane separation unit is composed of a series of flat-sheet membranes (see Figure 2). Pressurized feed water is introduced on one side of the membrane, and the trans-membrane pressure pushes the water through the membrane itself. The data presented in this report was generated using 2 membranes, which corresponds to 0.43 m² of active membrane area. Due to the modular nature of the membrane unit, adding more membranes to the system is done by stacking more membranes inside the module. The membranes are separated from each other using a polypropylene spacer material with a thickness of 2.5 mm; this spacer has two functions: 1) physically separate the



Figure 3. Hollow fiber membrane module used in study (www.Toray.com).

membranes from each other to allow water to flow through the module; and, 2) induce turbulent flow conditions between the membrane sheets that reduces the thickness of the cake layer forming on the membrane surface during filtration.

Hollow fiber membrane module: PVDF hollow fiber membrane modules (MWCO 50 kDa) with a total surface area of 0.2 m² were used in an outside-in configuration (Figure 3); no air scouring was used during the treatment process.

Spiral wound membrane module: A spiral wound membrane module containing PAN membranes (MWCO 75 kDa) with a surface area of 3.1 m² was tested as an off-the-shelf option for larger scale applications (Figure 4). In this module, the membrane leaves are separated by thicker polypropylene spacers (3 mm) so as to be able to accommodate the granular fluid – the result of filtering a high concentration Pickering emulsion.

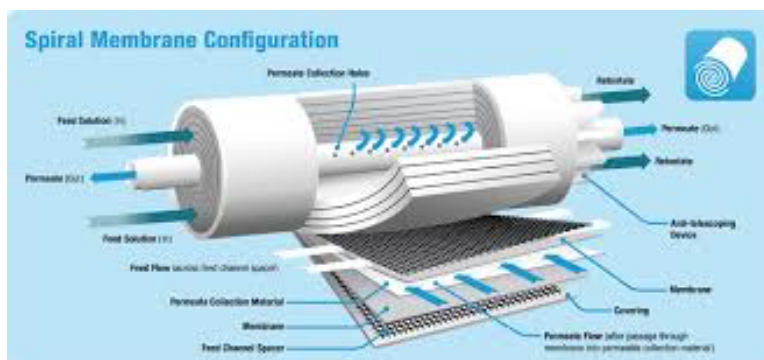


Figure 4. Schematic of spiral-wound membrane module used in study (www.kochmembranes.com)

Magnetic separation unit: A magnetic drum separator was purchased from Prab Inc. (Kalamazoo, MI). These machines are typically used to recover ferrous shavings from cutting fluids, and are composed of a chain-driven rare-earth permanent magnet drum and a rubber roller. Membrane retentate was introduced to the magnetic separator where it came in contact with the rotating magnetic drum; NPs were collected by the rotating drum, and the rubber roller was used to press water and oil from the NPs. The remaining fluid, containing oil and water, was removed from the separator using gravity. The separated NPs, oil and water were returned to the feed tank to complete the recycling loop. A graphical description of the magnetic separation process can be seen in Figure 5.

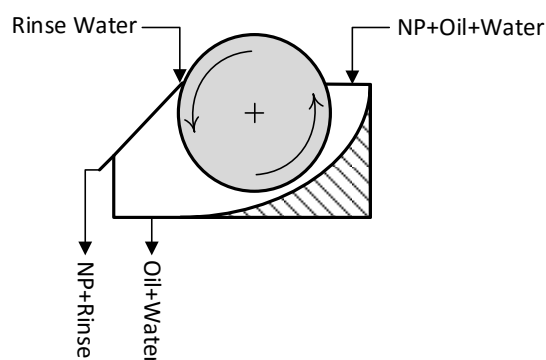


Figure 5. Magnetic drum separator used to recover and reuse NP from the concentrated retentate.

Water and material characterization

Membrane permeate was analyzed using a total organic carbon (TOC) analyzer and chemical oxygen demand (COD) measurements to characterize the performance of the membranes in terms of oil removal. The ability of the magnetic separator to recover the NPs from the membrane retentate was determined by collecting a certain amount of NPs from the magnetic drum (after being squeezed by the roller), extracting the crude oil with hexane (X3) and

measuring the extracted oil concentration using a UV-vis spectrophotometer (absorption at 350 nm). To test the recovery efficiency of the magnetic separator in terms of NP recovery, a small volume of fluid from the magnetic separator was placed in a vial and exposed to a rare earth magnet, followed by the decanting of the vial (while the magnet was still held to the vial). NPs remaining in the vial were collected and weighed.

Results and Discussion

Stability of Pickering emulsions

TOC analysis of the water column after Step 1 of the experimental method indicated that a significant amount of crude oil emulsified into the aqueous phase, with a mean value of 540 ± 214 mg/L (Figure 6a). This value was used as the baseline measurement to determine the effectiveness of the particle stabilization method, i.e. any oil removal from the aqueous phase was measured relative to this value.

Magnetite stabilization

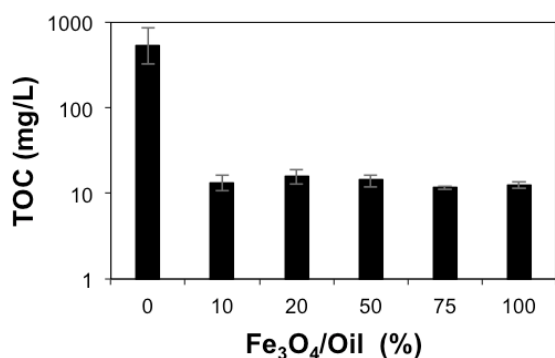


Figure 6a. TOC concentrations in the water phase as a function of NP/oil ratio. Notice that the Y-axis is in log scale.

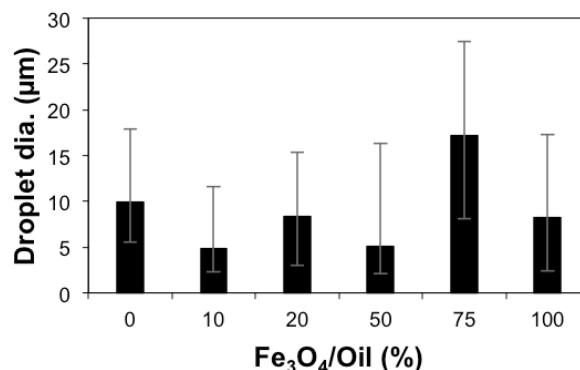


Figure 6b. Oil drop size distribution of magnetite stabilized ANS crude oil.

For the magnetite NPs, we tested a range of concentrations as described in the Materials and Methods section. TOC analysis of the aqueous phase demonstrated that above a ratio of 0.5:1 the oil concentration in the oil phase was consistently below 15 ppm (Figure 6a). Microscope image analysis indicated that the addition of magnetite NPs did not significantly change the average droplet diameter (Figure 6b). The addition of magnetite NPs changed the appearance of the emulsion, transforming the droplets from clear to black, indicating that the NPs have partitioned to the oil/water interface (Figure 7). Additionally, it is clear that the NPs are somewhat aggregated, and do not form a very smooth coating around the oil drop, leading to the irregular shapes observed as the magnetite concentrations increase. Images of the sample vials containing the settled Pickering emulsions demonstrate the effectiveness of the emulsification method (Figure 8). As can be seen, increasing concentration of magnetite NPs lead to a decrease in the cloudiness of the mixture (indicating oil removal) as well as any remaining oil floating on the surface; floating oil looks like brown spots floating in the water/air interface. Some residual

stabilized droplets can be seen floating in the high concentration (1:1 magnetite to oil ratio) vial. These can be easily removed with a magnet, indicating that they are in fact stabilized oil drops and not “free” oil.

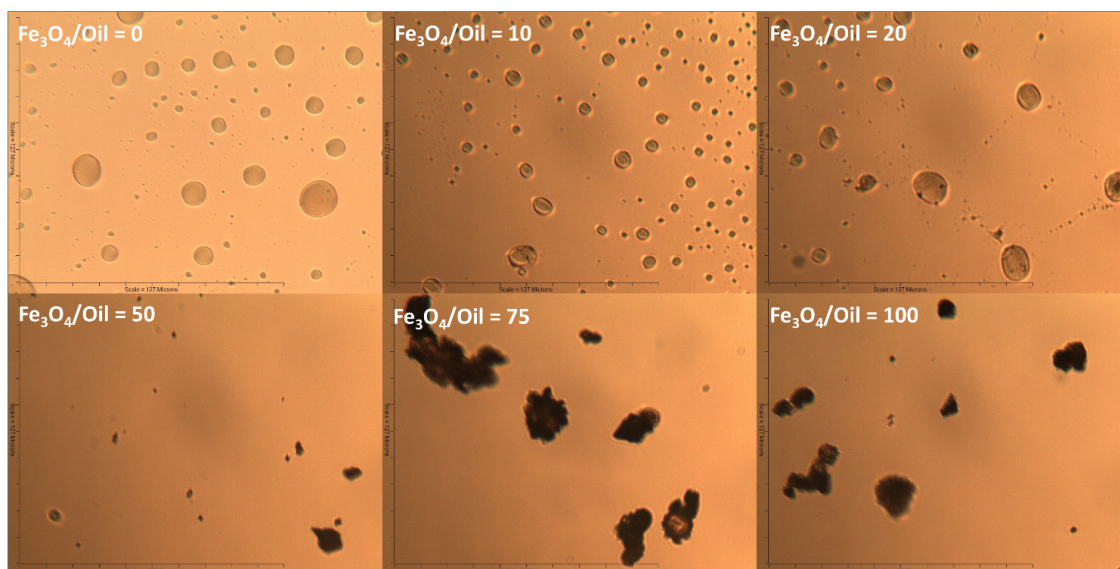


Figure 7. Optical microscope images of plain and magnetite-coated ANS crude oil drops. Each image is a representative picture corresponding to a different magnetite/oil ratio.

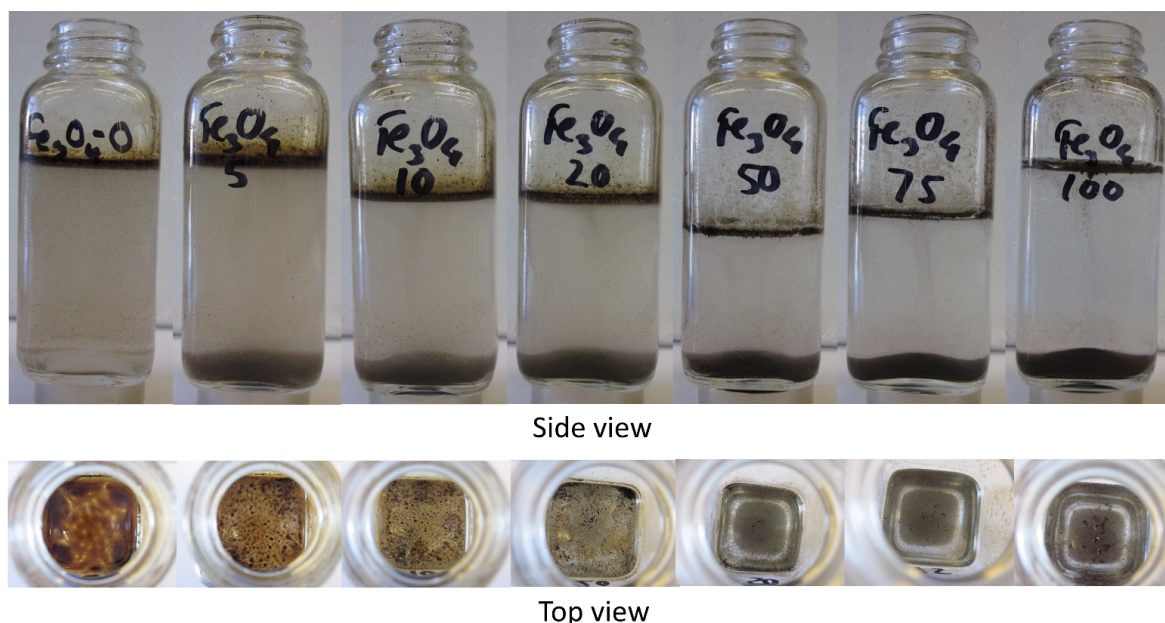


Figure 8. Images of oil/water mixture sample vials demonstrating the change in solution optical properties as a function of magnetite concentration. From left to right 0, 5, 10, 20, 50, 75, and 100% magnetite/oil ratio.

Maghemite stabilization

Results for maghemite were quite similar to those obtained for magnetite, which is not surprising considering their similar chemical structure and size. TOC analysis demonstrated that very little oil was left in the water phase once maghemite particles were added to the solution (Figure 9a), with TOC values dropping below 10 ppm. Optical microscope image analysis demonstrated that there was no significant change in oil drop size (Figure 9b and 10). Images of the sample vial demonstrate that increasing maghemite concentrations result in decreasing amounts of “free” oil floating on the surface as well as a decrease in sample turbidity (Figure 11).

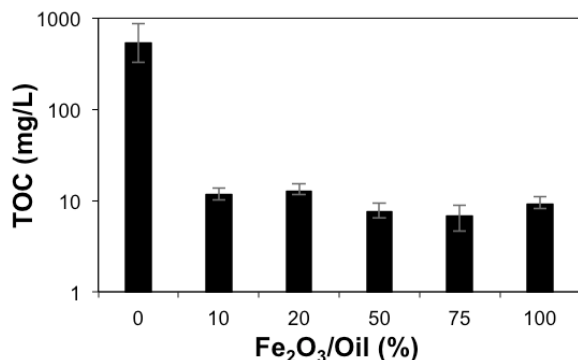


Figure 9a. TOC values as function of maghemite concentration.

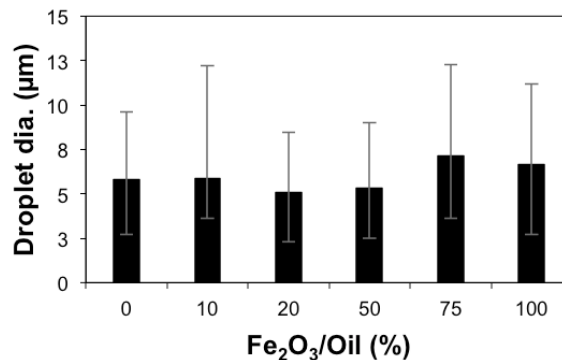


Figure 9b. Oil drop diameter as a function of maghemite loading.

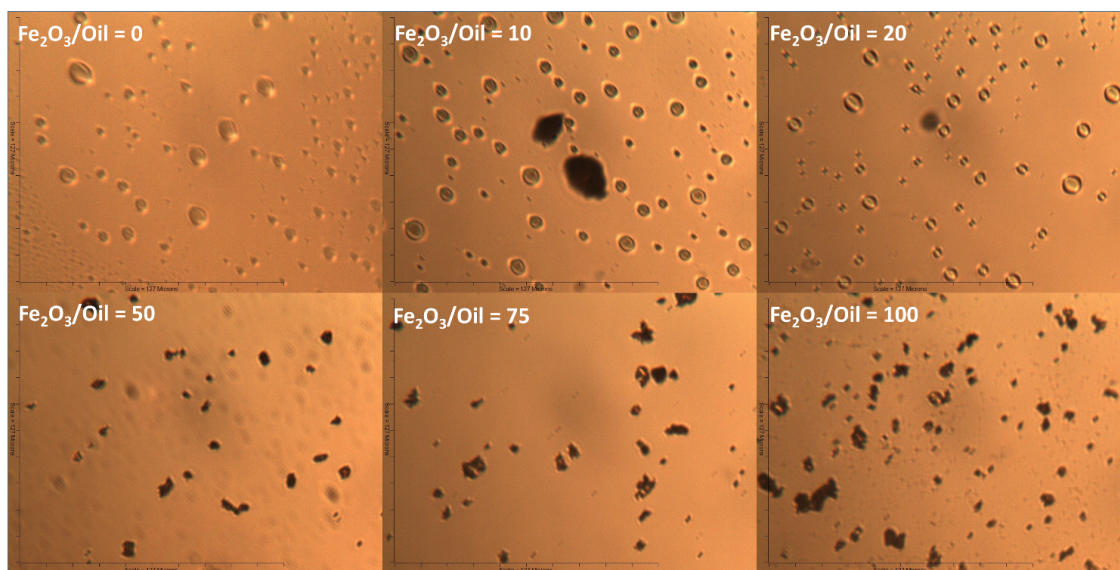


Figure 10. Representative optical microscope images of oil droplets as the maghemite concentration increases.

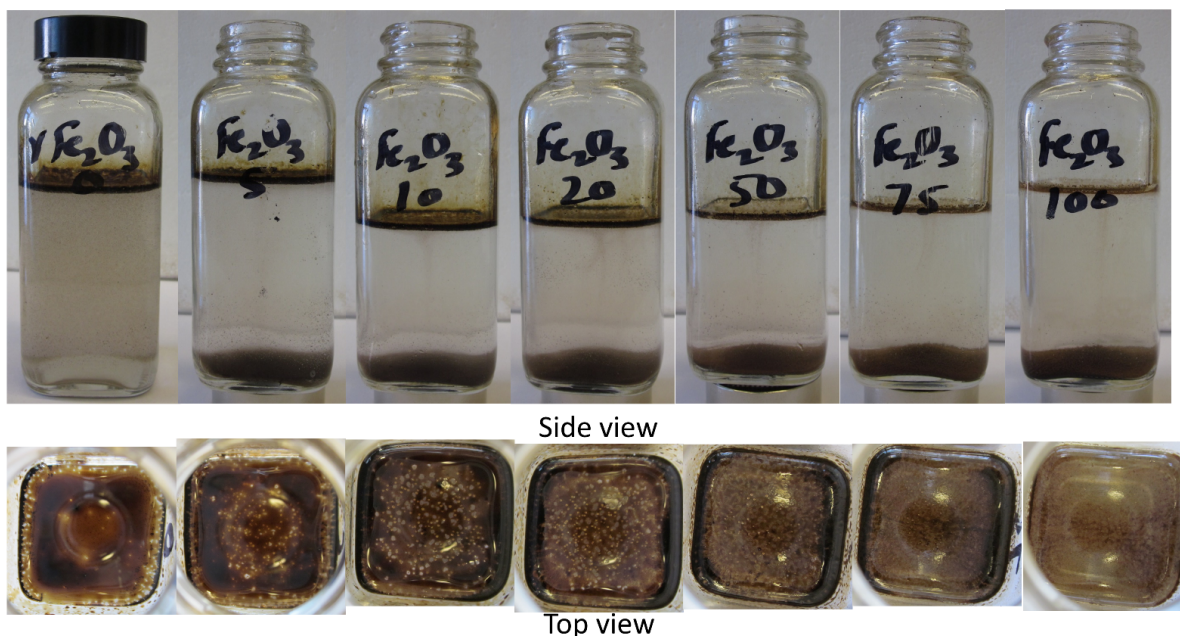


Figure 11. Images of ANS crude oil in sample vials as a function of maghemite concentrations. From left to right 0, 5, 10, 20, 50, 75, and 100% maghemite/oil ratio.

Carbonyl iron stabilization

Once again, TOC analysis demonstrated that the CI was very effective at removing the oil from the aqueous phase (Figure 12a). Surprisingly, the average droplet size seems to decrease with the addition of CI particles, although the results are not statistically significant (Figure 12b and 13). Similarly to the previous results for magnetite and maghemite, increased CI concentrations beyond 50% w/w yield a consistently transparent aqueous phase as well as an oil-free air/water interface (Figure 14).

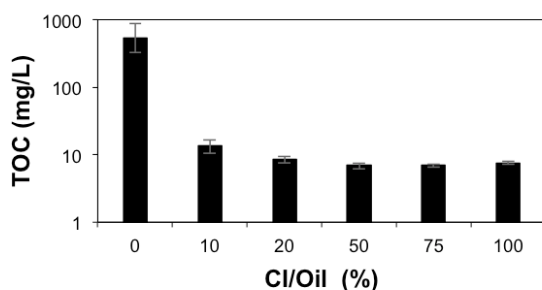


Figure 12a. TOC measurements in the aqueous phase as a function of CI concentration

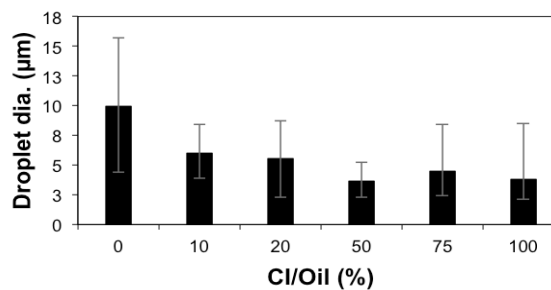


Figure 12b. Droplet size as a function of CI concentrations.

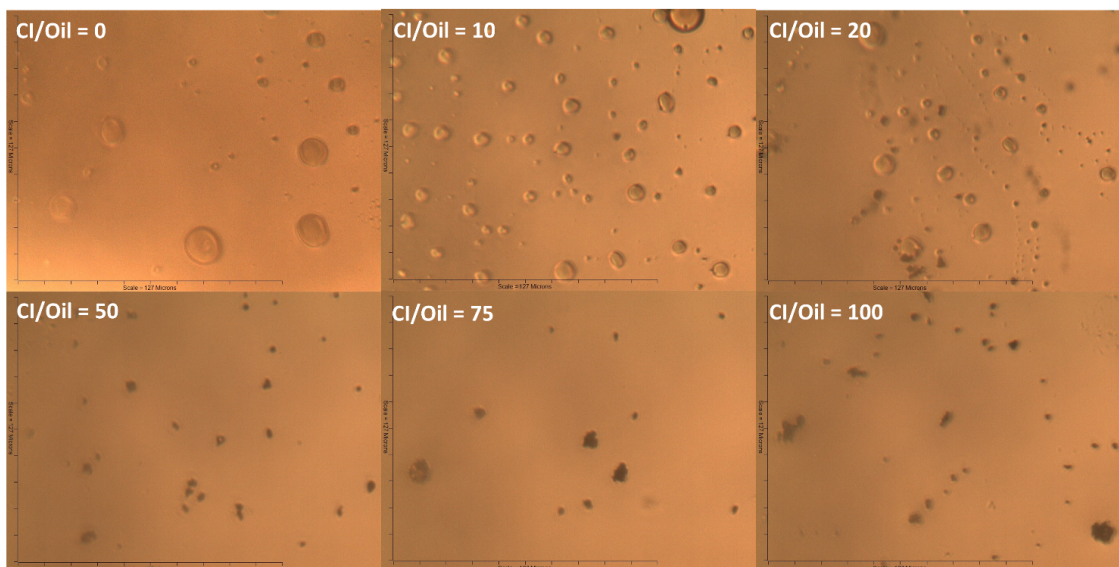


Figure 13. Optical microscope images of CI stabilized ANS crude oil drops as a function of CI concentrations.

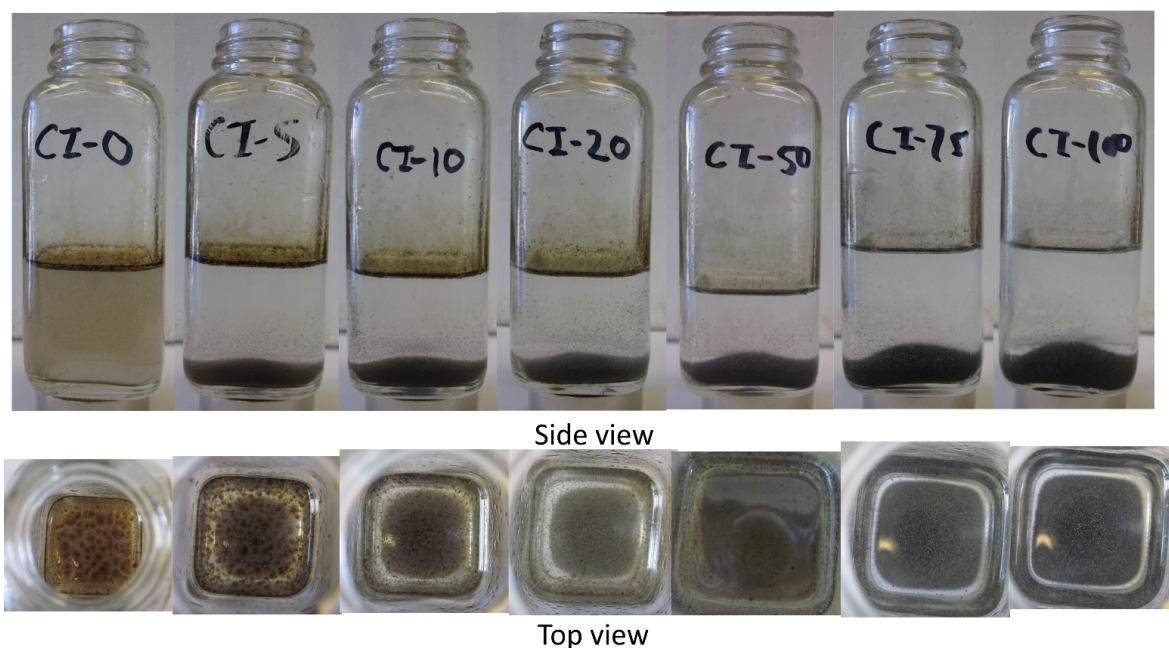


Figure 14. Images of ANS crude oil in sample vials as a function of CI concentrations. From left to right 0, 5, 10, 20, 50, 75, and 100% CI/oil ratio.

Scanning electron microscope image analysis of NP-stabilized oil

A clearer picture of the oil/NP structure was enabled through the use of SEM. Due to the high vacuum used in this form of microscopy, the stabilized oil drop was heavily sputtered with a layer of gold to prevent the oil from evaporating during the analysis. As can be seen, magnetite NPs form a smooth and continuous shell around the oil drop (Figure 15). The size of the drop is

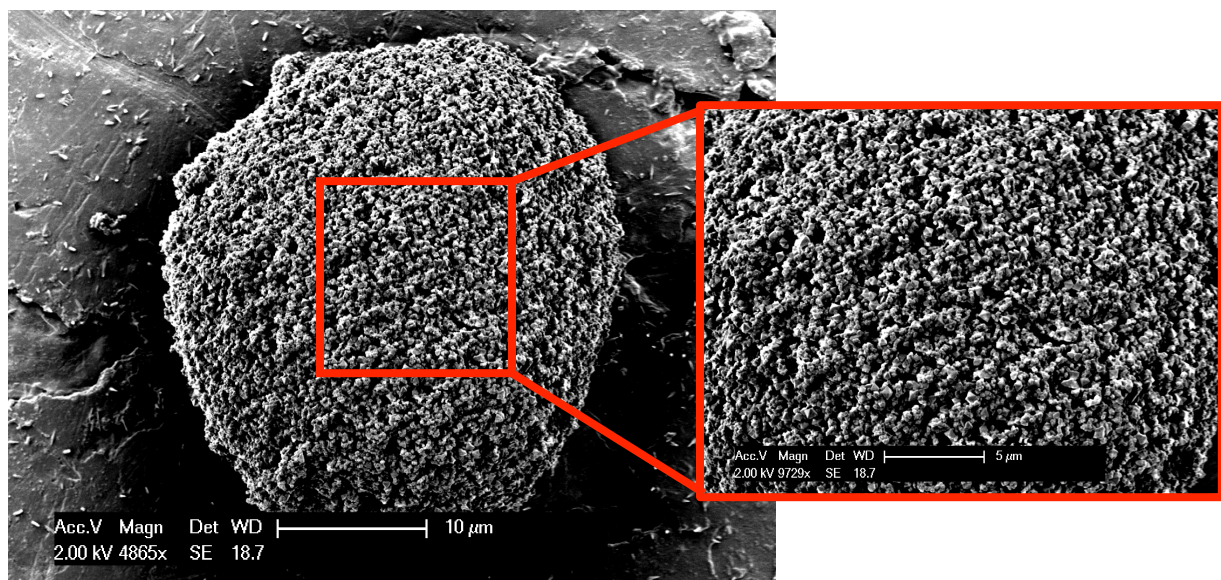


Figure 15. SEM images of magnetite stabilized crude oil drop. Inset is a zoomed-in image demonstrating the tight packing of the NPs on the oil drop surface.

consistent with the sizes observed using the optical microscope. We hypothesize that the closeness and completeness of the magnetite NP covering is what prevents neighboring oil drops from coalescing, and is ultimately responsible for the enhanced system performance during the membrane separation step of the treatment process.

The lowest feasible NP/oil ratio was determined to be **50%** (w/w) for all particles tested (magnetite, maghemite, and CI). At this ratio, the aqueous phase was consistently free of organics, and the water/air interface was free of floating oil. Below this concentration, we are concerned about the presence of “free” oil floating on the surface, although the aqueous phase is still organic free. Furthermore, image analysis demonstrated that the addition of particles did not significantly change the average oil drop size, although the addition of sufficient numbers of particles did remove any oil from the system, once the particles were allowed to settle, indicating that all of the oil was trapped in the Pickering emulsion. High resolution image analysis (SEM and optical microscopy) demonstrated that the oil drops are completely covered with a continuous coating of NPs. This coating prevents the oil from neighboring drops from “feeling” each other, and prevents coalescence.

Magnetic separator performance

We tested the performance of the magnetic separator in terms of its ability to separate the oil from the NPs. It was determined that ~18% (by weight) of the oil remained in the NPs after the magnetic drum separator, indicating a removal rate of 82% (Figure 16). We tested the ability of the recovered NPs to form new Pickering emulsions, and observed that the NPs were indeed capable of forming new, stable emulsions. Thus, the system achieves steady state, where 82% of the oil is recovered, and 18% of the oil is carried by the NPs back to the feed tank, where they form new emulsions with the fresh incoming (and non-stabilized) crude oil in seawater.

Furthermore, we evaluated the amount of NPs in the oil/water mixture coming out of the separator, and we found that 6% (by weight) of the NPs remained in this stream. This means that in a real deployment of the system, small amounts of NPs will need to be periodically replenished. The recovery of NPs can likely be improved by using a stronger permanent magnet that will attract more NPs to the rotating drum.



Figure 16. Recovered NPs from the magnetic drum separator. These NPs contain only 18% of the oil that was originally trapped in them, and they can be reused indefinitely to form new emulsions.

Flat sheet membrane performance

The UF membranes operated in a flat-sheet configuration were successful in treating the oil-contaminated feed at fluxes as high as 50 LMH over long periods of time with no significant membrane fouling observed. However, due to the viscous nature of the Pickering emulsions and their relative density, the Pickering emulsions tended to deposit inside the membrane module. While this did not cause any appreciable fouling, the feed water to the membrane system eventually ran clear (as the system was run in full recycling mode). To prevent this from occurring, the membranes required periodic backwashing, which removed the deposited material and prevented material losses in the module itself.

Initial tests of the flat sheet membranes were conducted without the magnetic separator. In these experiments, the retentate and permeate were returned to the feed tank at the same rate, ensuring constant concentrations in the system. The system was tested at high fluxes (100 LMH) using two NP/oil ratios (w/w) – 0.5, and 1, with a crude oil concentration in the feed tank of 10 g/L, and the system operating at 90% recovery, which means the oil concentration in the membrane module was 100 g/L (Figure 14). As can be seen, the system exhibited no fouling over a period

of 24 hours when the NP/oil ratio was 1:1, but some fouling was observed when the ratio dropped to 0.5:1 (as exhibited by the rise in trans-membrane pressure (TMP), Figure 17). Thus, it was concluded that optimal system stability required a NP/oil ratio of 1:1, which was maintained throughout the rest of the experimental work.

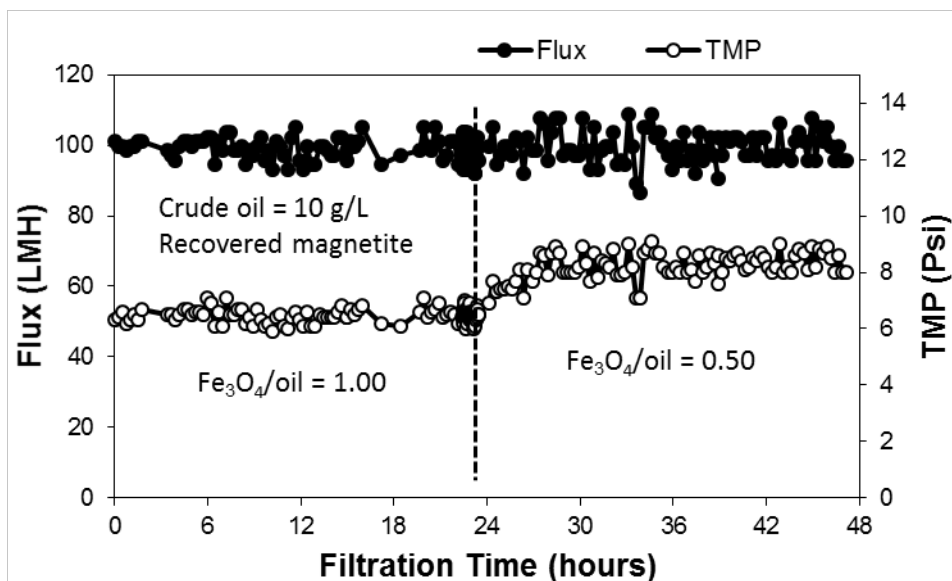


Figure 17. Impact of NP/oil ratio on membrane performance. In this set of experiments, the magnetic separator was not used to recover the NPs.

While successful at operating at these high fluxes (100 LMH) with no NP recovery system, the system experienced significant fouling at fluxes as low as 70 LMH when the magnetic separator was added to the treatment process, even when processing less oil – 3 g/L oil in the feed tank (30 g/L in the module; Figure 18). The addition of the magnetic separator and the resulting recycling and reuse of the NPs is critical for process sustainability. Thus, for any real applications, the magnetic separator must be considered as a critical part of the separation process, and any limitations added by it must also be considered. It is likely that the Pickering emulsions formed from the repeatedly recycled NPs are not as stable, which leads to the observed membrane fouling at 70 LMH. Alternatively, it is possible that the Pickering emulsions formed from the recycled NPs are not homogeneous, and may contain some bare oil on their outside surface that comes into contact with the membrane surface.

In contrast to the poor performance observed at 70 LMH, the flat sheet membranes were capable of operating at 50 LMH with no significant fouling over prolonged periods of time (Figure 15). Here, the membranes were backwashed for 2 minutes every hour with permeate and the cross-flow velocity was 30 cm/s, with the system operating at 90% recovery and at a constant flux (3 g/L in the feed and 30 g/L in the module), with pressure increases are associated with membrane fouling.

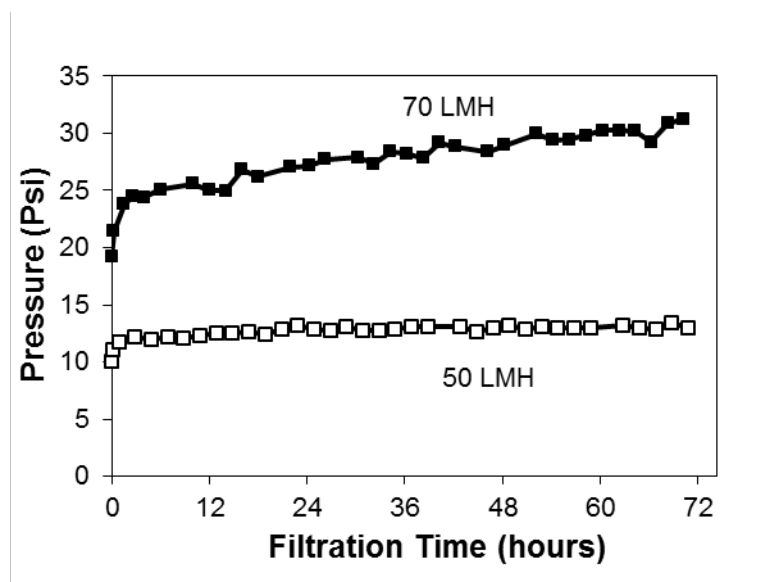


Figure 18. Flat sheet PAN UF membrane performance at 50 and 70 LMH with the magnetic separator used to recover and reuse the NPs. Experimental conditions were 3 g/L in feed (30 g/L in module), cross flow velocity of 30 cm/s, backwash for 2 minutes every one hour.

Hollow fiber membrane performance

The hollow fiber UF module replaced the hollow flat sheet module described in the previous section; all other systems (magnetic separator, pumps, and control hardware) were kept the same. The hollow fiber membranes did not perform well in the separation of oil and water, and we were not able to operate the system effectively. Membrane fouling occurred under all experimental conditions, with fluxes as low as 30 LMH resulting in irreversible fouling, even with frequent backflushing (2 minutes with permeate, every 30 minutes; Figure 19).

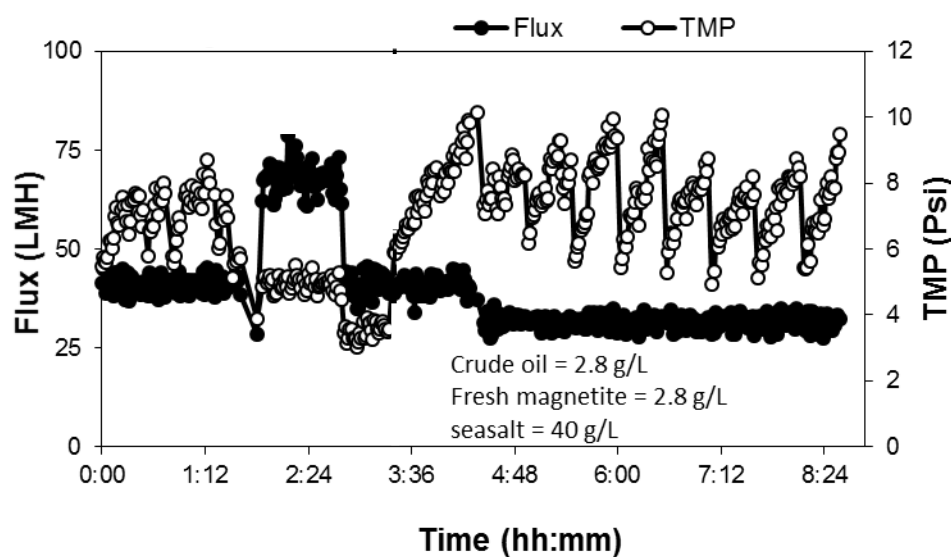


Figure 19. Hollow fiber PVDF membrane performance. System was operated at constant flux (40 and 30 LMH), with frequent backwashing (2 minutes every 30 minutes with permeate).

We speculate that the irreversible membrane fouling observed under these conditions stems from two primary reasons. The first reason is the poor flow conditions and relatively poor performance of the backflushing mechanisms, a result of the tight packing of the hollow fiber membranes in the module, which resulted in visible NP/oil accumulation on the fibers themselves (the pressure vessel was made of transparent polycarbonate). The second potential reason is the more hydrophobic nature of the PVDF material, which can result in increased membrane wetting by the oil in the Pickering emulsion [4].

Spiral wound membrane performance

A large, commercially available PAN UF membrane in a spiral wound configuration was tested for its ability to separate the NP-stabilized oil from the seawater. The system was operated using similar operating conditions to those in previous systems (30 cm/s, 3 g/L in feed and 30 g/L in module, 90% recovery). The relatively narrow flow channel in the spiral wound element (2.5 mm) resulted in significant deposition of the Pickering emulsions. To minimize this deposition, the membrane required frequent backwashing (1 minute every 10 minutes with permeate). Once frequent backwashing was implemented, deposition was minimized, and the system operated smoothly. The membrane was tested at different fluxes with excellent performance observed (little fouling) at fluxes as high as 70 LMH over long periods of continuous use (Figure 20). As can be seen, the pressure required to maintain the constant flux (30, 50, and 70 LMH) did slowly increase over time, with pressure increasing from 12 to 14 psi (16% increase), from 15 to 21 psi (40% increase), and from 20 to 26 psi (30% increase) for the 30, 50 and 70 LMH cases, respectively, over a period of several days. However, the membrane could be recovered once prolonged backwashing was implemented (Figure 21), indicating that over very long periods of time, there is some accumulation of deposited material in the system that requires more prolonged backwashing (beyond the one minute backwashing events used in this series of experiments). As can be seen, the membrane loses permeability (compared to the pristine membrane) after it was used to separate the oil from the seawater (at 30 LMH) and then recovered by backwashing and cross-flushing for 20 hours with tap water; after running the membrane at a higher flux (50 LMH), the membrane was again flushed and backwashed with tap water and it was observed that the permeability did not change, indicating that irreversible fouling did not occur, despite the increase in the pressure requirements during the experiment (Figure 21). In fact, the initial deposition of the Pickering emulsion can be seen in the relatively fast increase in pressure during the initial stage of filtration (first few hours) followed by a very gradual increase. This indicates that a cake layer is being formed on the membrane surface, which can be removed with a prolonged backwashing.

The rate of volume of treated water using the spiral-wound membrane module was 195 L/hr at 70 LMH. Due to the modular nature of spiral wound elements and the fact that these modules are commercially available makes the prospect of system scale-up highly plausible. Furthermore, the compact nature of spiral wound membrane modules makes the deployment of this system possible on the confined space available on skimming vessels.

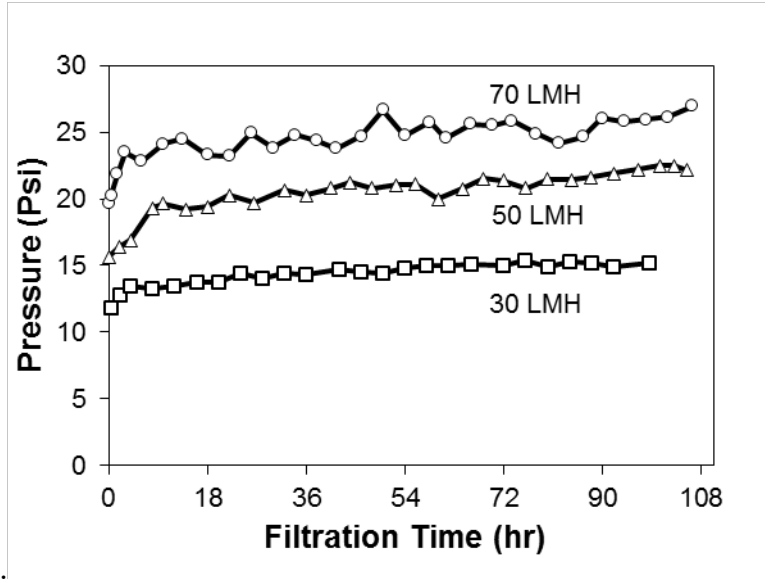


Figure 20. Spiral wound UF PAN membrane performance at different fluxes. Experimental conditions were 3 g/L in feed (30 g/L in module), cross flow velocity of 30 cm/s, backwash for 1 minute every 10 minutes with permeate.

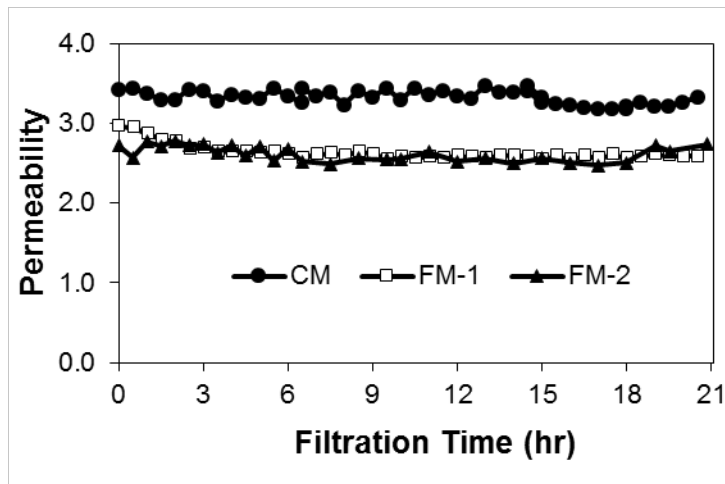


Figure 21. Permeability of pristine (CM) spiral wound PAN UF membrane; permeability after running at 30 LMH (30 g/L in module) for 100 hours and rinsed with tap water (FM-1); permeability after running at 50 LMH (30 g/L in module) for 105 hours and rinsed with tap water (FM-2).

Water quality of membrane permeate



Figure 22. From left to right: crude oil in seawater, crude oil + magnetite NPs (Pickering emulsion), settled Pickering emulsion (after 24 hours settling), and membrane permeate

The UF membranes used in this study all had MWCO values that were far below the sizes of the Pickering emulsions – 75 kDa and 150 kDa for the PAN and PVDF materials, respectively. As such, it was expected that these UF materials would be able to reject nearly all oil, producing extremely high permeate quality. COD measurements of membrane permeate from all membrane systems was persistently below 15 ppm, with an average of 7 ± 3 ppm, and a turbidity of 0.1 NTU. At these values, water can be safely discharged with no further treatment. An image of crude oil in seawater, the Pickering emulsion, and membrane permeate can be seen in Fig. 22, demonstrating the poor water quality of the membrane feed, and the effectiveness of the membrane treatment system.

Conclusions

We have demonstrated the effectiveness of our novel membrane-based oil/seawater separation method by treating highly contaminated seawater. Crude oil was successfully encapsulated using three different iron oxide particles (magnetite NPs, maghemite NPs, and carbonyl iron microparticles) to form micron-sized and highly stable Pickering emulsions. The Pickering emulsions were stable over prolonged periods of time. The Pickering emulsions were created using a simple mixing step with the aid of a paddle mixer, and were used as feed for the UF membrane system.

The membranes were successfully operated at reasonably high fluxes (up to 70 LMH) with no irreversible fouling observed under certain membrane configurations. Flat sheet UF PAN membranes were successfully operated at 50 LMH and spiral wound UF PAN membranes were successfully operated at 70 LMH, but PVDF UF membranes in hollow fiber configuration suffered from irreversible fouling even at low fluxes. In all cases, Pickering emulsion deposition in the flow cell required frequent backwashing to remove the cake layer. However, up to a given flux, the formation of the cake layer did not result in irreversible fouling of the PAN membranes. The PVDF membranes did irreversibly foul, likely due to the higher hydrophobicity of the membrane material, which led to enhanced membrane wetting by the crude oil from the emulsion. In all cases, membrane permeate was oil free, with a COD <15 ppm, allowing for easy discharge of the permeate in compliance with existing environmental regulations.

The NPs used to form the Pickering emulsions were successfully recovered, recycled and reused through the use of a magnetic drum separator. The magnetic drum separator was used to remove NPs from the membrane retentate, producing a stream of highly concentrated oil, and nearly oil-free NPs that were reused to form new Pickering emulsions. The magnetic separator recovered 94% of the NPs, with the remaining 6% in the concentrated oil stream. A rubber roller was used to squeeze oil out of the NPs, with the oil concentration in the recovered NPs being 18% by weight.

The oil/water separation method presented here can be used to further concentrate oil recovered through the use of skimming devices, which will reduce on-board ship storage currently needed to hold oil-contaminated water that is collected during skimming operations. Alternatively, the method described here can be used to remove the emulsified oil fraction that remains in water after the free oil is decanted. Regardless of how the system is used, it will significantly increase the operational range and efficiency of oil skimming vessels, since they will require less frequent stops to discharge contaminated water at on-shore storage facilities.

Recommendations

In light of the successful demonstration of our approach towards oil/seawater separation, the following recommendations can be made:

1. The integrated oil/seawater separation method demonstrated in this project can be used to remove both emulsified and free oil from water, producing a treated water stream with COD concentrations below the current discharge limit that can be safely and legally discarded overboard.
2. The compact nature of the system makes it ideally suited for deployment on skimming vessels, with the goal of reducing response fleet storage needs. If after the mechanical separation step (e.g. decanting) the residual oil concentration in the collected water aboard the skimming vessel is 1 g/L (a worst-case scenario), our technology can reduce storage needs by 97%.
3. The high cost associated with the replacement of NPs lost during the magnetic separation step renders this oil/seawater separation method impractical as the primary separation step onboard skimming vessels.
4. The scalable nature of membrane-based separation processes, coupled to the widespread availability of the systems (membranes, magnetic drum separator, mixing tanks) used in this process, makes the scaling up and deployment of this technology a promising possibility. Furthermore, due to the evolving nature of water quality regulations governing the discharge of contaminated water from skimming vessels, membrane-based separation methods are the only reliable technology capable of guaranteeing the water quality parameters of discharged waters, since water quality parameters of discharged waters can be tuned by selecting membranes with different rejection properties. The use of Pickering emulsions to stabilize crude oil and prevent fouling during membrane treatment makes the use of multiple membrane types (i.e. ultrafiltration, nanofiltration) a real possibility.

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